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UNIQUE PROPERTIES OF NEW ALKALI EARTH PHOSPHORS SENSITIVE TO INFRARED RAYS

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As early as 1943, while investigating the phosphorescence of Ca.S. SrS+ Ce, Sm, the suggestion was made [4] that ultraviolet light not only activates phosphors but, as in the case of the $ZnS;O_2$ + Mn phosphor, accelerates the phosphorescence, i. e., acts as if "red." (The mechanics of phosphorescence of typical phosphors, to which alkali earth phosphors also belongs, is a recombining one [1], i.e., during activation, in general, ionization of the centers of phosphorescence takes place, but not conversion into an activated state. During activation Se, Sm or Eu, Sm phosphors acquire new properties [2,3].) This permits clarification of one paradoxical phenomenon (in a thick layer of phosphor), consisting of a sudden shift in the time between the growth of the phosphorescence at the time of activation and a simultaneously delayed growth of flash property. A strict demonstration of the presence of the accelerative action of the activating light on this phosphor was carried out only recently by Morgenshtern [5] and on the phosphor SrS; Eu, Sm by Trapeznikova [6].

If an activating light accelerates phosphorescence, even at comparatively weak intensities, E will reach the limit L_∞ of the accumulated light sum L. But the existence of one such limit is not sufficient in itself to prove the accelerative action of the activating light as it may be brought about by different causes.

First, it can be assumed that, under conditions of the experiment, all centers of phosphorescence are ionized and consequently further growth of L is impossible, in spite of an increase in the intensity of the activating light E; second, the activating light not only induces, but also

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extinguishes phosphorescence, which sets a limit for the increase of L; third, there is in the phosphor a limited number of local levels, and when they are all shown to be filled with electrons, further growth of L is obviously impossible; and fourth, the cited activating light may also function simultaneously as if "red."

In the first case, we have the well-known equation expressing the change in the concentration n of the ionized centers (the light sum L is obviously proportional to the concentration of the ionized centers n) of phosphorescence (or photoelectrons, which amounts to the same thing, inasmuch as the number of photoelectrons is equal to the number of ionized centers) during time

$$\frac{dn}{d\vartheta} = -pn^2 + E\ (N-_n), \qquad (1)$$

where p is a constant, proportional to the probability (1) of recombination in a unit of time during the concentration of the ionized centers, and equals one; N is the concentration of all centers of phosphorescence (both ionized and nonionized).

Under activation, where equilibrium is established between absorption and radiation, dn/d = 0 and when the intensity of phosphorescence $I = pn^2$, it is found that, in a state of equilibrium

$$I_{\infty} = E(N-n_{\infty}).$$

It follows from this equation that when E is large, and n_{∞} is comparable with N, the linear relationship between I_{∞} and E is disturbed. In the experiment, however, for the cited alkali earth phosphors I_{∞} was at all times proportional to E, (It should be noted that, in the majority of cases, there was no fluorescence proportional to E that could affect the readings.), even when n_{∞} (I_{∞}) reached the maximum value n_M (I_M). Hence, under ~~the conditions of the experiment, it was always true that~~

$$n \ll N. \qquad (2)$$

In the second case, taking into consideration the relation (2) and the pr ..ce of extinction, there appears in the place of (1)

$$\frac{dn}{d\vartheta} = -pn^2 - \chi E_n + EN, \qquad (3)$$

where χ is a certain coefficient of proportionality, allowing for extinction. Obviously, this term must be proportional to both E and n.

Since $I = pn^2$ and, during full activation $dn/d\vartheta = 0$, it follows from (3) that

$$I_{\infty} = E(N - \chi n_{\infty}).$$

If extinction plays an important role, χn_{∞} should be comparable with N, but in that case there would be another disturbance of the linear relationship between I_{∞} and E which is contrary to the experiment.

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In the third case, if we start from the equations evolved by Adirovich [7] for extinction, and supplement them with the term allowing for activation, there is obtained for n an equation analogous to (3). The difference is the fact that in this case the term $\chi E n$ does not give the number of "decaying" centers of phosphorescence but allows for the filling of local levels with electrons. As before the term pn^2 gives the number of recombinations made possible by the electrons released from local levels.

Since now, in contrast to the former equation $I = pn^2 + \chi E n$ it follows from (3) that, during full activation ($dn/d\vartheta = 0$)

$$I_\infty = EN,$$

i.e., I_∞ is proportional to E.

The dependence of N_∞ on E is given by equation (3) when $dn/d\vartheta = 0$. If there are introduced new normalized variables $\bar{n}_\infty = \frac{\chi n_\infty}{N}$ and $\bar{E} = \frac{\chi^2 E}{pN}$,

$$\bar{n}_\infty = \sqrt{\frac{\bar{E}^2}{4} + \bar{E}} - \frac{\bar{E}}{2} \tag{4}$$

(It is curious to observe that from equation (1) the dependence of $\bar{n}_\infty$ on $\bar{E}$ is the same, only the normalizing factors will be different.) In such a normalization for small values of $\bar{E}$ the magnitude when

$$\bar{n}_\infty = \sqrt{\bar{E}} \quad \text{when } \bar{E} \to \infty \; \bar{n}_\infty \to 1 .$$

In the fourth case, the equation for n, unlike (1) and (3), will not contain a term, linear in relation to n, but on the other hand, the magnitude p will consist of two parts: p_0, the proportional probability of recombination, dependent on electrons released from the local levels by the thermal method (probability of "thermal" recombination), and αE the electrons released by the optical method by activation (probability of "optical" recombination),

$$\frac{dn}{d\vartheta} = -(p_0 + \alpha E)n^2 + EN. \tag{5}$$

If there is introduced here in place of (4) the normalized variables $\bar{n} = n/\sqrt{N}$ and $\bar{E} = \alpha E/p_0$ there shall similarly be obtained.

$$\bar{n}_\infty = \sqrt{\frac{\bar{E}}{1+\bar{E}}} . \tag{6}$$

 [redacted]

Just as before, for small values of E the magnitude $\bar{n}_{\infty} = \sqrt{E}$ when $\bar{E} \to \infty \; \bar{n} \to 1$.

The difference between (4) and (6) lies only in the central part of the curve $\bar{n}$ ∞ in the function derived from E, as graphically shown in the previously mentioned work of Morgenshtern [5], where these curves are compared with experimental results. The latter can conform only to a theoretical curve (6).

The presence of an accelerative action of an activating light is corroborated also by interesting experiments made by Morgenshtern. It was shown that it was possible to observe an immediate flash upon the action of an activating light and that the limiting magnitude n_M is dependent on the wavelength λ of the activating light. These results cannot in any way be reconciled with the fact that the limit n_M is dependent on the filling of all (deep) local levels by electrons. Otherwise, this would imply that $n_M = m_o$ where m_o—is the concentration of local levels. In that case m_o would also be a function of λ which seems hardly probable.

The experiments of Trapeznikova [6] with phosphor SrS ∤ Eu, Sm serve as direct proof of the accelerative action of activating light and the absence of an extinguishing effect.

The new phosphors have one more noteworthy property, the magnitude of the light sum is very much dependent on the method of obtaining it [8,9]: with optical (L_r), i.e., infrared light excitation, the magnitude can sometimes be greater than with thermal (L_T), i.e., the heating of phosphor. Morgenshtern [9] showed that this is due to the fact that the probability of recombination with radiation for the electron released by the optical method, for CaS.SrS∤Ce,Sm phosphor is five times greater than in the case of thermal activation. (According to data just published by Morgenshtern, the picture is approximately the same for SrS∤Eu,Sm phosphor.)

It follows from the experiments of Trapeznikova and Morgenshtern that the light sum L_g determined from the curves of the growth of phosphorescence, in case of activation by optical light, is equal to L_r but, where the activation is ultraviolet light, it is from one and one half to two times less than L_r.

The lower effectiveness in recombination with radiation for ultraviolet light may be dependent on the fact that under conditions of the experiment where the ultraviolet is weaker in comparison with the visible light, a large part of the thermal electrons is involved in recombination. According to the work of Morgenshtern [9], this must lead to a diminution of the output of phosphorescence.

The presence of thermal electrons in the process of the growth of phosphorescence can be seen from the results of Trapeznikova. It follows from his experiments that, in repeated activation, after the temporary process is extinguished, the luminous intensity I is, at least at first, of an order less than the limit I ∞, although, at the same time, the light sum n [sic] is shown to be less than the limit, but only by a few percent. (Such a process must be dependent upon the presence of small local levels [5, 10].) On the other hand I very quickly reaches the value I ∞ (growth of the temporary process). This shows that, on the one hand, for electrons, the probability of recombination is far less than the probability of localization and, on the other hand, that the rapid growth of phosphorescence is caused by thermal or, perhaps even optical (activating light) reverse activation of electrons accumulated at the time when this process developed. The abrupt growth of I, i.e., the number of recombinations, cannot be dependent on the growth of n, inasmuch as n always increases by only a few percent.

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The smaller n is, the smaller the probability of recombination and the larger the probability of localization, which, of course, increases the share of the thermal electrons, and therefore correspondingly diminishes the output of phosphorescence. According to Trapeznikova's data, during activation by ultraviolet light, I_E was one half of that of activation by optical light, which, according to the foregoing, should have diminished the output of phosphorescence during activation by ultraviolet light.

In conclusion, it may be mentioned that the new phosphors have many interesting properties and unusually complicated processes of phosphorescence, and, though it may seem paradoxical, it is due precisely to these complicated processes that it is sometimes possible to clarify certain details of the phenomenon, which can hardly be successfully studied in ordinary phosphors.

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